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To cite this version:

P. Lethuillier, J. Chaussy. Sign change of the c.e.f. parameters in light rare earth compounds in relation with the delocalization of the 4f shell. Journal de Physique, 1976, 37 (2), pp.123-127. <10.1051/jphys:01976003702012300>. <jpa-00208394>

HAL Id: jpa-00208394
https://hal.archives-ouvertes.fr/jpa-00208394
Submitted on 1 Jan 1976

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SIGN CHANGE OF THE C.E.F. PARAMETERS IN LIGHT RARE EARTH COMPOUNDS IN RELATION WITH THE DELOCALIZATION OF THE 4F SHELL

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(Reçu le 10 septembre 1975, accepté le 7 octobre 1975)

Résumé. — Le schéma des niveaux de champ cristallin de composés intermétalliques RX₃ (R = Ce, Pr, Nd ; X = In, Pb) a été déterminé par des mesures de susceptibilité et de chaleur spécifique ; une expérience de diffusion inélastique de neutrons a été réalisée pour NdIn₃. Le paramètre de champ cristallin A₀⁴ r⁴ > des composés du cérium est positif ; il décroît pour les composés du praséodyme et devient négatif pour les composés du néodyme. Le paramètre de champ cristallin A₀⁶ r⁶ > présente une variation similaire du praséodyme au néodyme. Ce changement de signe des paramètres de champ cristallin semble être relié à la faible différence d'énergie entre la bande de conduction et les niveaux 4f au début de la première série des terres rares.

Abstract. — The crystal field level scheme of RX₃ (R = Ce, Pr, Nd ; X = In, Pb) intermetallic compounds has been determined by fitting susceptibility curves and specific heat Schottky anomalies; an inelastic neutron diffraction experiment has been performed for NdIn₃. The fourth order C. E. F. parameter A₀⁴ r⁴ > of the cerium compounds is positive; it decreases for the praseodymium compounds and becomes negative for the neodymium compounds. The sixth order C. E. F. parameter A₀⁶ r⁶ > exhibits the same trend to negative values from praseodymium to neodymium compounds. This sign change of the C. E. F. parameters appears to be related to the small energy difference between the conduction band and the 4f levels at the beginning of the first rare earth series.

1. Introduction. — The compounds R (Sn, Pb, In, Tl, Pd)₃, where R is a rare earth, have the cubic AuCu₃ type-structure. They have been extensively studied [1 to 11]. It is interesting to determine the crystal field parameters of these compounds so as to understand their physical properties (such as the superconducting transition temperature of La₁₋ₓPrₓX₃ solutions [12] or the electrical resistivity [13]) and also in order to understand the interaction between the 4f electrons and the conduction band. These parameters have been mainly determined by the analysis of susceptibility and specific heat measurements.

In these compounds, the rare earth is situated on a site with cubic symmetry. The crystalline electric field (C.E.F.) splits the ground multiplet of the rare earth ion and the level scheme is described by two C.E.F. parameters A₀⁴ r⁴ > and A₀⁶ r⁶ > or similarly, following Lea et al. [14], by W and x.

(*) This work is a part of the thesis of P. Lethuillier.

The magnetic susceptibility of this ion is then given by the formula:

\[
\frac{1}{\chi} = \frac{1}{\chi_{C.F.}} + n
\]  

(1)

where \(n\) is the molecular field coefficient and \(\chi_{C.F.}\) is the crystal field susceptibility:

\[
\chi_{C.F.} = N g^2 \mu_B^2 \sum_{i,j} \left[ \frac{\langle i | J_z | i \rangle^2}{kT} + \frac{2\langle i | J_\perp | j \rangle^2}{E_j - E_i} \right] \times \exp \left( \frac{-E_i}{kT} \right)
\]

\(|i\rangle\) and \(|j\rangle\) are the eigen functions of the hamiltonian defined in reference [14] and the energies \(E_i\) are the eigen values.
The Schottky-type specific heat is given by the formula:

$$C_M = \frac{R}{Z} \left[ \frac{\sum f_i (E_i)}{kT} \exp \left( \frac{-E_i}{kT} \right) - \frac{1}{Z} \left( \frac{\sum E_i f_i}{kT} \exp \left( \frac{-E_i}{kT} \right) \right)^2 \right]$$

where $f_i$ is the degeneracy of the level of energy $E_i$.

2. Experimental. — The susceptibility measurements have been performed in a magnetic field of 1.7 kOe between 2 and 300 K. The error bars are ± 0.2 K on the temperature in the whole range; the precision on the magnetic susceptibility is one per cent with a minimum error of ± 0.3 x 10^-4 e.m.u./mole.

All these compounds melt congruently. As they oxidize rapidly, the samples are stored under vacuum.

3. Results. — The Néel and paramagnetic Curie temperatures and the paramagnetic moments of these compounds are given in the table I.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\theta_N$ (K)</th>
<th>$T_N$ (K)</th>
<th>$\mu_{\text{eff}}$</th>
<th>$\mu_{\text{th}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CePb$_3$</td>
<td>-17</td>
<td>2.54</td>
<td>2.54</td>
<td></td>
</tr>
<tr>
<td>PrPb$_3$</td>
<td>-8</td>
<td>0.35 (*)</td>
<td>3.58</td>
<td>3.58</td>
</tr>
<tr>
<td>PrIn$_3$</td>
<td>-9</td>
<td>3.72</td>
<td>3.58</td>
<td></td>
</tr>
<tr>
<td>NdIn$_3$</td>
<td>-12</td>
<td>3.78</td>
<td>3.62</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.75}$Nd$</em>{0.25}$In$_3$</td>
<td>-5</td>
<td>4</td>
<td>3.62</td>
<td></td>
</tr>
</tbody>
</table>

(*) Taken from reference [6].

3.1 CePb$_3$ (Fig. 1). — In the high temperature region, the susceptibility follows a Curie-Weiss behaviour with a paramagnetic moment very close to the trivalent ion value. Under 30 K, the magnetic susceptibility is not linear; at 4.2 K, the Curie constant is $C \approx 0.36$ instead of $C = 0.805$ for the free ion. The Curie constant corresponding to the isolated doublet is $C = 0.19$ and $C = 0.49$ for the quartet. We have fitted the experimental data with the formula (1). Unambiguously, the doublet is the lowest level. The best agreement is obtained with $W = 11$ K, $x = 1.0$ and $n = 18$ e.m.u. The fourth order term is then positive:

$$A_2^0 < r^2 > = 29 \text{ K}$$

3.2 PrPb$_3$ (Fig. 2). — This compound is a Van Vleck paramagnet [5, 6, 9]. The specific heat curve of PrPb$_3$ exhibits a lambda type anomaly at 0.35 K [6] which indicates a transition from antiferromagnetism to paramagnetism. The entropy under the lambda anomaly is about $R \ln 2$ showing that the ground state is the non-magnetic doublet $I_3$. Moreover it was found possible to fit the Schottky anomaly of CePb$_3$ versus temperature.

![CePb$_3$](image)

3.3 PrIn$_3$ (Fig. 3). — For this compound, the analysis of susceptibility and specific heat measurements [3, 4] has led to: $x = -0.7 \pm 0.1$, the corresponding value of $W$ being best determined by the $T = 0$ susceptibility of this Van Vleck paramagnet.

The Curie constant of this compound is larger than the free tripositive ion value, owing to the matrix contribution (Table I); the paramagnetic Curie temperatures of the RIn$_3$ compounds, given in the table I, have been determined with the experimental data corrected for the susceptibility of LaIn$_3$ measured by Toxen et al. [15]. The corrected susceptibility has been fitted with the formula (1). The best agreement is obtained with $x = -0.6 \pm 0.1$ (Fig. 3); the corresponding value of $W$ is: $W = 2.36$ K.

The second solution gives a susceptibility minimum (Fig. 2) which has not been observed. On the contrary, the first solution leads to a calculated susceptibility curve in perfect agreement with the experimental data: the fourth order term is then positive.

A similar analysis of the results of Bucher et al. [2] leads to the following C.E.F. parameters, for PrTl$_3$:

$$W = 1.6 \text{ K} , \quad x = -0.9$$

3.3 PrIn$_3$ (Fig. 3). — For this compound, the analysis of susceptibility and specific heat measurements [3, 4] has led to: $x = -0.7 \pm 0.1$, the corresponding value of $W$ being best determined by the $T = 0$ susceptibility of this Van Vleck paramagnet.

The Curie constant of this compound is larger than the free tripositive ion value, owing to the matrix contribution (Table I); the paramagnetic Curie temperatures of the RIn$_3$ compounds, given in the table I, have been determined with the experimental data corrected for the susceptibility of LaIn$_3$ measured by Toxen et al. [15]. The corrected susceptibility has been fitted with the formula (1). The best agreement is obtained with $x = -0.6 \pm 0.1$ (Fig. 3); the corresponding value of $W$ is: $W = 2.36$ K.
The determination of the C.E.F. parameters of this compound was performed with the use of three different techniques. An inelastic neutron diffraction experiment was performed on the spectrometer IN7 of the Institut Laue-Langevin at Grenoble. Details on the experimental technique are given in reference [10]. One spectrum was taken at 12 K, with an incident neutron energy of 40 meV; the counting time was two days. A broadened peak at 6 meV appears on the neutron energy loss side (Fig. 4). The width of this peak is about 10 channels whereas the spectrometer resolution is seven channels (full width at half maximum). If we refer to the level scheme given in reference [14], this means that the value of \( x \) is close to \( x = 0.37 \), where the levels \( I_6 \) and \( I_8^{(1)} \) cross. With an incident neutron energy of 10 meV, a small transition, corresponding to an energy of 0.5 meV, is visible. We give (Fig. 4), for comparison, the spectrum of the isostructural compound NdSn\(_3\), registered at 10 K. The oscillating background is due to imperfect calculator correlations. The first transition can be explained with the four sets of parameters:

- \( W = \pm 1.06 \text{ K}, \quad x = 0.43 \)
- \( W = \pm 0.91 \text{ K}, \quad x = 0.31 \)

The occurrence of the second transition excludes the solutions with \( W < 0 \).

In order to verify this result, we have measured, the heat capacity of NdIn\(_3\) and LaIn\(_3\). Between 20 and 300 K, the samples used for the experiment were cylinders of about 20 g. Our result concerning LaIn\(_3\) is in perfect agreement with previously reported measurements [4]. Between 20 and 30 K, the specific heat of NdIn\(_3\) slightly exceeds that of LaIn\(_3\) owing to the Schottky contribution (Fig. 5). Above 30 K, the opposite behaviour is observed because the Debye temperature is lower in LaIn\(_3\) than in NdIn\(_3\). At 20 K, the difference between the heat capacities of NdIn\(_3\) and LaIn\(_3\) is about 1.5 J/mole.K. The Schottky-type specific heat, calculated at this temperature with the formula (2) for the parameters determined above, is \( C_p \approx 1.7 \text{ J/mole.K} \) with \( W > 0 \) and \( C_p \approx 3 \) with \( W < 0 \). In this experiment also, the agreement is better with \( W > 0 \).
The susceptibility measurements of NdIn₃ and La₀.₇₅Nd₀.₂₅In₃ (Fig. 6) confirm the preceding results. In particular, between 2 and 5 K, the Curie constant of La₀.₇₅Nd₀.₂₅In₃ is C = 1.3 in agreement with the calculated values with \( W > 0 \) (with \( W < 0 \), the calculated Curie constant would be \( C = 1.1 \)).

Only two sets of parameters are possible, namely:

\[
W = 0.91 \text{ K}, \quad x = 0.31 \quad \text{or} \quad W = 1.06 \text{ K}, \quad x = 0.43.
\]

Thus the fourth and sixth order terms are negative as in NdPb₃ and NdSn₃ (10).

4. Discussion. — We have reported in the table II the values of \( W, x, A₂ < r⁴ > \) and \( A₆ < r⁶ > \) for RX₃ compounds (\( X = \text{In}, \text{Pb}, \text{Sn} \)) taken from references [3, 4], [10] and [11] or determined in this work. In CeIn₃ [4], specific heat measurements have shown that the doublet is the lowest state (\( A₄ < r⁴ > > 0 \) as in CePb₃), in agreement with our conclusions from magnetic susceptibility data. The variation of \( A₂ < r⁴ > \) and \( A₆ < r⁶ > \) with the rare earth ion has been represented on the figures 7 and 8 for RX₃ compounds (\( X = \text{In}, \text{Pb}, \text{Sn} \)). The C.E.F. parameters of the heavy rare earth compounds RIn₃ have been found negative [8] as those of the neodymium compounds NdX₃.

<table>
<thead>
<tr>
<th>TABLE II</th>
<th>C.E.F. parameters of the RX₃ compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W (\text{K}) )</td>
<td>( x )</td>
</tr>
<tr>
<td>CeIn₃ (*)</td>
<td>25</td>
</tr>
<tr>
<td>CePb₃</td>
<td>11</td>
</tr>
<tr>
<td>PrIr₃</td>
<td>1.6</td>
</tr>
<tr>
<td>PrIn₃</td>
<td>2.36</td>
</tr>
<tr>
<td>PrPb₃</td>
<td>-0.65</td>
</tr>
<tr>
<td>PrSn₃</td>
<td>~0</td>
</tr>
<tr>
<td>NdIn₃</td>
<td>{</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
</tr>
<tr>
<td>NdPb₃</td>
<td>1.26</td>
</tr>
<tr>
<td>NdSn₃</td>
<td>1.43</td>
</tr>
</tbody>
</table>

(*) Taken from reference [4].

It is well known that, for cerium compounds, the degree of localization of the 4f shell is smaller than for heavy rare earth compounds [16]. For instance, CeSn₃ becomes non-magnetic at low temperature [1] and CeIn₃ exhibits a Kondo effect [17]. For the praseodymium compounds, there are few published experimental data. We have shown recently, by resistivity measurements [13], that PrSn₃ exhibits a Kondo effect. Moreover, the exchange integral \( T \) between the 4f shell and the conduction band, as determined from the depression of the superconducting transition temperature, has been found much larger in Laₐ₋ₓPrₓX₃ solutions [2], [11, 12] than in Laₐ₋ₓGdₓSn₃ [18]. Thus, we may think that the observed sign reversal of the
C.E.F. parameters is related to the delocalization of the 4f shell at the beginning of the rare earth series. Chow [19] has shown that, in dilute alloys of heavy rare earths in Ag and Au, the 4f-5d interaction leads to an exchange correction to the direct Coulomb fourth order term, which reaches 85% of its value and is of opposite sign. In cerium compounds, as the 4f shell is not very far from the Fermi level, the 4f-5d overlap may lead to an exchange term larger than the Coulomb term, inducing the sign change of the fourth order term. It is interesting to observe that the case of praseodymium is intermediate between those of cerium and neodymium (Fig. 7 and 8).

Finally, it is remarkable that $A_{4}^{Q} \langle r^{A} \rangle$ and $A_{6}^{Q} \langle r^{B} \rangle$ vary similarly for the isoelectronic compounds RSn$_{3}$ and RPb$_{3}$; the variation of the fourth and sixth order terms of the RIn$_{3}$ compounds is larger than that of the RPb$_{3}$ and RSn$_{3}$ compounds.

Acknowledgments. — We thank Dr. J. Pierre for his help and Dr. E. Bucher for communicating unpublished results.

References